91602
new 82-10

COMPLIMENTARY COPY
Please Credit Ontario Hydro Research If
Reproduced in Whole or in Part

ontario hydro
research division

To: Dr. D. Mills
Director of Research

FIELD MEASUREMENTS OF NATURAL NO_x EMISSIONS FROM SOILS IN ONTARIO: BORDEN AND EGBERT - AUTUMN, 1989 AND SPRING, 1990

V.W. Middleton and G.L. Ogram
Environmental Physics & Chemistry Section
Environmental Sciences Department

ABSTRACT

Natural emissions of NO_x (NO and NO_2) from soils were measured at field sites located at Canadian Forces Base Borden (CFB Borden), Borden, Ontario and the Centre for Atmospheric Research Experiments (CARE), Egbert, Ontario during the late autumn of 1989. Measurements were also conducted at CARE during the spring of 1990. Measured NO emission fluxes at Borden were small and ranged from 0.04 to 0.47 ng(N) $m^{-2}s^{-1}$ over a two day period in late October, with diurnal average values of 0.09 and 0.21 ng(N) $m^{-2}s^{-1}$, respectively, for each of the two days. NO emission fluxes measured at Egbert a few days later were higher and ranged from 0.05 to 5.5 ng(N) $m^{-2}s^{-1}$ over a single diurnal cycle with a diurnal average flux of 1.5 ng(N) $m^{-2}s^{-1}$. Fluxes measured in spring at Egbert ranged from 0.04 to 1.9 ng(N) $m^{-2}s^{-1}$ for five days in late April and early May (diurnal averages ranged from 0.46 to 0.97 ng(N) $m^{-2}s^{-1}$). Emission fluxes of NO_2 during autumn, 1989, were occasionally of similar magnitude to the NO fluxes, in contrast to previously reported results, and to the measurements made during spring, 1990 at Egbert, where fluxes of NO_2 were generally much smaller than those of NO.

job	file	date	report no.
35-530	837.261	December 31, 1991	91-291-K

LEGAL NOTICE

This report was prepared by Ontario Hydro and, while effort has been made to assure the accuracy and applicability of the material contained herein, neither Ontario Hydro nor any person acting on its behalf:

(a) makes any warranty, express or implied with respect to the use of any information, apparatus, method or process disclosed in this report or that such use may not infringe privately owned rights; or

(b) assumes any liabilities with respect to the use of, or for damages resulting from the use of, any information, apparatus, method or process disclosed in this report.

1.0 INTRODUCTION

Atmospheric NO and NO_2 (referred to collectively as NO_x) participate in a complicated series of sunlight-initiated chemical reactions with various volatile organic compounds (VOC) to give rise to the net formation of photochemical oxidants, such as ozone (O_3) and peroxyacetylnitrate (PAN), which have been implicated in health effects and crop damage (Lin 1989, Melo et al. 1990). Human activities such as the use of fossil fuels and the combustion of biomass provide the major source of NO_x to the atmosphere. Significant production of NO_x also occurs as a result of natural processes such as lightning, natural forest fires, and biogenic emissions from soils. On a global basis, estimates of the contribution of natural sources vary widely from negligible to about one half of total NO_x emissions (Anderson and Levine 1987). Mackay (1988) averages estimates of NO_x sources from various references and obtains the following figures: of a total global tropospheric source term of 45 Tg(N) a^{-1}, about 63 % is anthropogenic, about 15 % is estimated to originate from soil, and the remaining 22 % is from other natural sources such as lightning and NH_3 oxidation.

Natural sources of VOC are also known to exist, such as trees which emit isoprenes and terpenes, which, compared to most other anthropogenic hydrocarbons, are highly effective in creating ozone. Natural background levels of NO_x and VOC therefore exist in the atmosphere and contribute to the natural background levels of atmospheric oxidants. Anthropogenic sources of NO_x and VOC act to perturb these natural levels of oxidants. However, it is difficult to clearly identify the role played by anthropogenic emissions as the chemistry of oxidant formation is complicated and non-linearly dependent on the concentrations of the precursor reactants. In simple terms, this means that increasing either NO_x or VOC concentrations will not necessarily lead to a corresponding proportional increase in oxidant concentrations. In fact, depending on already existing concentrations of these precursor species and other atmospheric conditions, addition of NO_x to the system can lead either to increased, decreased or essentially unchanged ozone levels (see, eg, Melo et al. 1990).

Oxidant levels averaged over large areas are, in general, expected to increase by the addition of anthropogenic pollutants. However, the relation between the amount of a pollutant released at a particular point and the oxidant levels resulting far downwind can be very complicated. Point emissions of NO, for example, may lead to a local reduction in ozone, due to the reaction

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (1)$$

but lead to enhanced O_3 production farther downwind, where NO_x can catalyze the formation of O_3 through reaction with VOC entrained into the plume.

Ontario Hydro's use of fossil fuels for electricity generation is a significant source of NO_x emissions in southern Ontario. These emissions may contribute to regional ozone episodes of the type observed frequently in the summer of 1988 (where the Canadian Air Quality Objective for Maximum Acceptable Level for O_3 (1 h average) of 82 ppbv (parts per billion by volume) was frequently exceeded).

A proposed control program for NO_x and VOC is currently under review in Canada. Rational decisions on the implementation of any emission controls directed at reducing oxidant levels require that the contributions of each source be defined and also that the effect of reducing emissions on ambient ozone levels be predicted (Melo et al. 1990). Because of the complexity of the atmospheric chemistry of ozone formation, it is necessary to rely on mathematical models, which describe oxidant formation, transport and depletion on a regional basis, in order to estimate the impact of a source, or set of NO_x sources, on oxidant levels. In order to have confidence in using the predictions of such models it is important to ensure that models are sufficiently realistic in their treatment of key processes.

In this regard, a knowledge of the natural emissions of key reactants is necessary in order to correctly model the regional impact of anthropogenic NO_x emissions. Natural emissions occur over large regional scales and form the "chemical background" into which anthropogenic pollutants are emitted. However, very few measurements of natural NO_x and VOC emissions have been available for Ontario.

An experimental program was therefore initiated to gain information on natural NO_x emissions in southern Ontario. To date, field measurements under various conditions have been reported by Mackay and Ogram (1989) and Headon et al. (1990). Shepherd et al. (1991) recently have reported measurements of fluxes from fertilized agricultural soils in Ontario.

The present report documents the results of chamber measurements of natural nitric oxide (NO) and nitrogen dioxide (NO_2) emissions from soils at Canadian Forces Base Borden (CFB Borden), Borden, Ontario, and the Centre for Atmospheric Research Experiments (CARE), Egbert, Ontario, during late October, 1989, and also at CARE during April and May, 1990. These results provide further information on seasonal variations of NO_x emissions and of the differences between a forest site and an open field site.

The field studies are being conducted in parallel with a series of laboratory measurements (by the Biological Research Section of Ontario Hydro Research Division) on soil samples taken from various sites chosen to be representative of major soil types and land use categories of southern Ontario. It is hoped that these laboratory measurements can supply information on regional variations in NO_x emission rates. Soil samples were also taken from the Egbert and Borden experimental field sites and will be tested in the laboratory to ensure that the laboratory measurements give representative fluxes.

2.0 EXPERIMENTAL METHODS

2.1 Flux Chamber

The NO_x flux measurement procedure was based on the closed chamber technique employed by various groups in Europe and the USA (Johansson and Granat 1984, Parrish et al. 1987, Williams et al. 1987, Anderson and Levine 1987). The apparatus was field tested at CARE in 1988 (Mackay and Ogram 1989) and was used for further measurements at CARE during the summer

of 1989 (Headon et al 1990). Figure 1 is a schematic of the experimental arrangement. A closed, flow-through chamber was used. The chamber was in the shape of a cube with 30 cm sides, and was constructed of polycarbonate sheet lined internally with Teflon. A small fan was mounted within the chamber to ensure mixing of the chamber atmosphere.

"Zero" air was generated by drying ambient air and passing it through a chamber containing a UV lamp and charcoal trap, which removed NO_x and O_3 from the air stream. The "zero" air supply stream from a calibrator (Monitor Labs Inc. Model 8550) was used for this purpose. This "zero" air was pumped into the chamber at 5 L min^{-1} (rate confirmed by a calibrated mass flow meter) giving a time constant for gas exchange in the chamber of approximately 5 min. The chamber was vented directly to the atmosphere. The NO_x and NO_2 levels in the vent flow were therefore characteristic of the values in the well-mixed chamber atmosphere and were measured using a Luminox LMA-3 NO_2 analyzer and LNC-3 NO converter. The sample air flow (approximately 1.5 L min^{-1}) was taken from a "T" junction on the vent line. For calibration purposes, a flow of NO standard gas (9.53 ppmv, nominal, of NO with about 0.11 ppmv NO_2 impurity, Matheson) was diluted in the "zero" air stream from the calibrator. Details of the calibration procedure are given in Headon et al. (1990), Appendix C.

The chamber was mounted on a steel, Teflon-lined skirt which was driven into the soil. The chamber could be raised and lowered automatically on a predetermined schedule to allow automated operation. The "zero" air stream could be switched by stainless-steel solenoid valves to bypass the chamber completely. Bypassing the chamber enabled scrubbed air to be sampled to check the instrument zero. Automation of the system allowed unattended flux measurements to be taken for 24 h to observe diurnal trends.

In the automated set-up, all data were collected by a data logger (Campbell 21X). The data logger generated and stored 2 to 5 min averages of data sampled every 5 s. The logged data consisted of thermocouple measurements of soil temperature (both inside and outside the chamber), barometric pressure, relative humidity (inside the chamber) and air temperature (inside the chamber). One minute averages of the LMA-3/LNC-3 output, taken every 5 s, were also output to final storage. The LNC-3 NO converter was switched between the NO_2 and NO_x (NO plus NO_2) mode every three minutes.

A second data logger, synchronized to the first, was used to control solenoid valve switching and chamber raising and lowering. The NO_x analyzer calibration was checked at a single point (corresponding to about 10 ppbv NO) before and after each test. External air temperature and relative humidity were recorded and observations of weather conditions were made.

During automated operation the test cycle was as follows. The chamber was lowered into place for a period of one hour during which period the emission flux was measured. The emission fluxes were calculated using NO_x concentrations averaged over the last twenty minutes of the chamber "down" period. The chamber was then raised to allow the soil plot to re-equilibrate with ambient humidity and temperature. During the chamber "up" period the ambient concentrations of NO_2 and NO_x were recorded over a period of thirty-five minutes. The solenoid

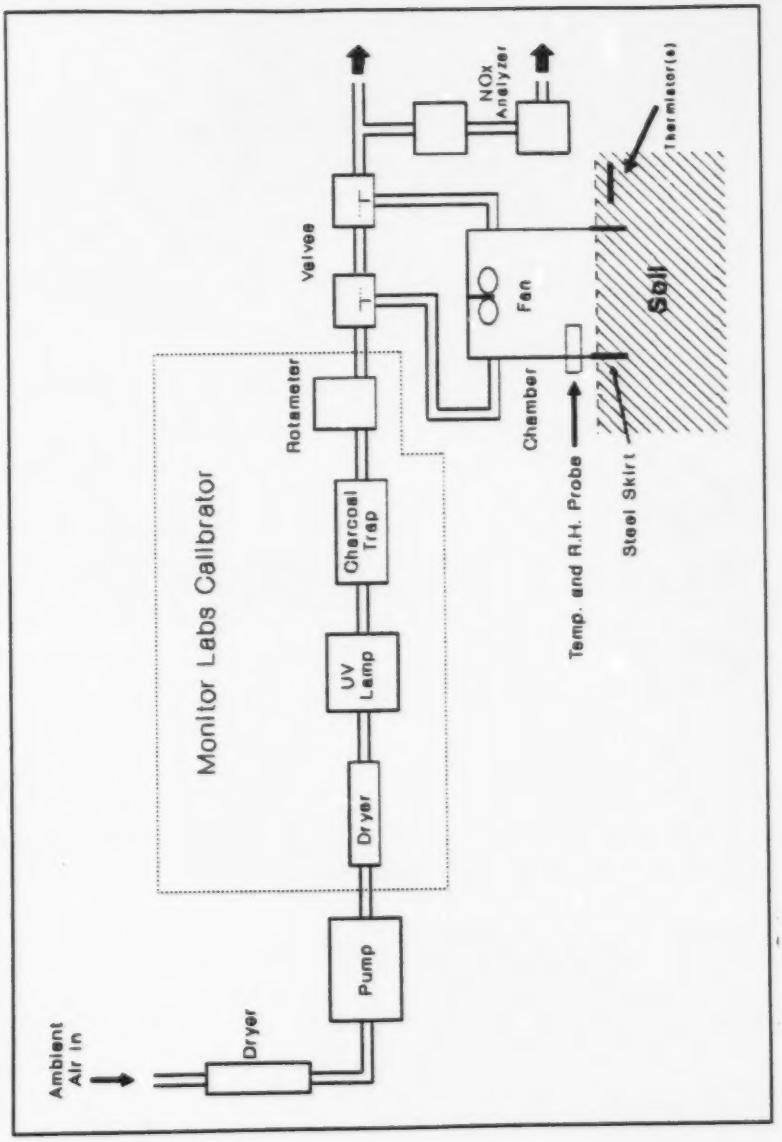

Figure 1. Schematic of the flow-through chamber apparatus for measuring emission fluxes of NO_x from soils.

valves were then switched to check the "zero" air over a period of twenty-five minutes, thereby completing the one-hour "up" cycle. After one hour in the "up" position the chamber was again lowered and the cycle repeated. In this manner, fluxes, averaged over a period of about 20 min, were measured at two hour intervals.

The NO and NO_2 fluxes were calculated from the steady state concentrations of NO and NO_2, respectively, reached in the chamber near the end of the chamber "down" period, as follows:

$$J(NO) = [NO]\ Q / A; \tag{2a}$$

and,

$$J(NO_2) = [NO_2]\ Q / A; \tag{2b}$$

where J is the emission flux, Q is the flow rate through the chamber, A is the area of soil exposed to the chamber, and [NO] and $[NO_2]$ are the concentrations of the respective species in the chamber air.

It was not uncommon for the instrument zero to drift over a range of about 0.2 ppbv during the diurnal cycle. Measured NO_x levels in the chamber were adjusted by subtracting the "zero" reading that was closest in time. However, because flux measurements and the zero determinations were usually about one hour apart, flux values of below about 0.12 ng(N) $m^{-2}s^{-1}$, which corresponds to a chamber concentration of approximately 0.2 ppbv, should be considered unreliable.

2.2 Field Tests

The tests were conducted at two field sites operated by the Atmospheric Environment Service of Environment Canada: the forest research site located at Canadian Forces Base Borden, near Angus Ontario; and the Centre for Atmospheric Research Experiments (CARE) at Egbert, Ontario.

The Borden site is a mixed deciduous forest, primarily composed of aspen and maple. Further details of this site are given by Neumann, et al. (1989). At the time of the October experiments, the canopy had experienced complete leaf fall. Prior to the study, snow fall had occurred. However, experiments were conducted at above freezing temperatures at the beginning of an Indian Summer period with temperatures reaching a high of about 20°C during the day and declining to a few degrees celsius during the night (Edwards 1991).

The experiments at CARE were conducted on a field of mixed grasses and alfalfa located to the west of the CARE laboratory buildings. The experimental plots were located nearby the sites used for previous measurements (Mackay and Ogram 1989, Headon et al. 1990). Conditions during the measurements of April 22 to May 3, 1991, were generally fair, with temperatures well

above normal during the middle of the period. Air temperatures declined near the end of the test period and fell below freezing during the nights of May 2 and May 3.

The experimental sites at Egbert were prepared by using a sharp blade to cut the surface vegetation to below 1 cm in height (being careful not to uproot the vegetation during this procedure). The Borden sites had extensive forest leaf cover which was carefully removed without disturbing the underlying turf. The steel chamber skirt was then inserted into the ground, while attempting to disrupt the surrounding soil as little as possible.

For each plot, soil cores were taken to a depth of 10 cm both from the test plot and immediately adjacent to the test plot. The samples from the test plot were taken after the completion of the test, and samples adjacent to the plot were taken during the test run. All soil samples were analyzed for bulk density (dry mass per unit volume of soil) and water content. Additional soil samples were sent to Agri-Food Laboratories and Land Resource Sciences, University of Guelph, for soil chemistry and texture analysis. All samples were kept frozen until analyzed. The results of soil analysis are given in Appendix A.

3.0 RESULTS AND DISCUSSION

Table 1 summarizes the Borden and Egbert test results as follows: test site; test number; test date; test start time (local time); NO emission flux, J(NO), and its relative standard deviation (calculated from the variation in [NO] over the flux measurement period); and NO_2 emission flux, $J(NO_2)$, and its relative standard deviation (calculated in a similar way to that for NO). Also given are chamber air temperature and relative humidity, soil temperature within the chamber (at approximately 1.5 cm depth), and the ambient NO_x concentrations.

Over all tests, measured NO emission fluxes ranged from about 0.04 to 5.4 ng(N) $m^{-2}s^{-1}$, with NO_2 fluxes ranging from below 0.01 to 4.1 ng(N) $m^{-2}s^{-1}$. (As discussed in the previous section, values below about 0.1 ng(N) $m^{-2}s^{-1}$ should be considered unreliable). As found previously, (Headon et al, 1990) fluxes followed a diurnal cycle. The highest fluxes occurred during the day and fluxes were generally much lower at night.

Measured fluxes of NO at the Egbert site for the periods studied here (late autumn and spring) ranged from 0.08 to 5.4 ng(N) $m^{-2}s^{-1}$. Previous studies at the same site during the summer and late summer (July to September) of 1989 gave values ranging between 0.3 and 10.7 ng(N) $m^{-2}s^{-1}$ (Headon et al, 1990); ie, of similar order to, but somewhat higher in magnitude than, the values found in the present study.

Table 2 shows fluxes averaged over the diurnal cycle. Diurnally averaged fluxes for both NO and NO_2 ranged over about 0.1 to 1.5 ng(N) $m^{-2}s^{-1}$. Fluxes measured at the forest site in late October, 1989 were generally lower than those measured at Egbert.

Figures 2 to 5 show the NO and NO_2 fluxes plotted against soil temperature for all the tests that covered a diurnal cycle. Soil temperature is also plotted because previous studies have indicated

TABLE 1

Soil NO_x Emission Fluxes

Location	Sample	Start Date	Run #	Start Time	J(NO)	STD J(NO)	$J(NO_2)$	STD $J(NO_2)$	Cham. Air Temp.	Soil Temp.	Ambient $[NO_x]$
Borden	1	23/10/89	1	1412	0.16	3.9	0.16	3.7	16.4	8.5	7.4
			2	1612	0.12	2.4	0.14	2.2	14.9	9.2	6.7
			3	1812	0.07	4.4	0.14	1.3	12.0	9.1	6.3
			4	2012	0.10	0.0	0.13	0.0	10.9	8.9	6.8
			5	2212	0.09	11.7	0.13	3.7	9.0	8.4	6.5
			6	12	0.17	1.6	0.09	4.2	9.2	8.2	3.7
			7	212	0.04	0.0	0.09	0.0	8.6	8.0	3.6
			8	412	0.04	19.5	0.09	3.4	7.6	7.7	3.1
			9	612	0.04	6.8	0.07	5.8	7.0	7.4	2.5
			10	812	0.05	12.7	0.06	5.3	7.8	7.3	3.0
Borden	2	24/10/89	1	1817	0.29	4.0	0.07	22.1	13.8	11.2	23.5
			2	2017	0.44	2.3	0.10	8.4	11.9	10.6	33.7
			3	2217	0.47	3.4	0.10	7.4	10.7	10.1	25.4
			4	17	0.22	4.4	0.08	5.3	9.8	9.7	7.2
			5	217	0.20	5.5	0.03	43.6	9.0	9.2	5.5
			6	417	0.12	12.2	0.04	12.8	8.6	8.9	6.1
			7	617	0.12	11.6	0.04	32.8	8.3	8.6	2.8
			8	817	0.06	38.8	0.03	70.8	8.4	8.4	2.6
			9	1017	0.10	11.0	0.01	49.5	13.9	9.3	3.7
			10	1217	0.12	75.9	0.60	17.5	22.6	11.3	1.5
			11	1417	0.11	34.0	0.50	2.2	23.6	12.6	0.0
Egbert	1	30/10/89	1	1845	2.25	27.6	4.15	8.5	12.9	13.6	51.1
			2	2045	1.37	9.6	1.67	3.1	10.1	12.0	20.2
			3	2245	0.89	5.2	0.33	3.4	9.2	11.1	13.5
			4	45	0.94	4.3	0.09	22.1	7.9	10.2	14.2
			5	245	0.68	5.2	0.17	11.2	7.2	9.5	18.9
			6	445	0.80	4.3	0.16	21.8	8.3	9.3	11.0
			7	645	0.80	7.2	0.54	7.1	8.7	9.4	12.6
			8	845	1.31	13.1	1.55	3.5	14.0	10.9	16.8
			9	1045	5.45	11.0	4.03	6.2	18.8	12.8	42.0
			10	1245	0.55	31.2	2.68	4.7	18.4	14.2	0.0
Egbert	2A	19/04/90	1	1039	0.71	7.4	0.48	13.3	22.1	9.4	1.0
			2	1239	0.53	5.5	0.09	14.7	22.3	11.9	2.2
			3	1439	0.45	4.8	0.16	9.8	23.5	13.3	2.5
Egbert	2B	22/04/90	1	1405	0.66	1.8	0.10	10.6	24.9	15.8	1.2
			2	1605	0.93	1.7	0.12	7.8	26.7	16.9	1.2
			3	1805	0.96	1.2	0.00	223.1	18.2	15.1	1.5
			4	2005	0.72	2.0	0.00	6.3	12.2	13.1	2.0
			5	2205	0.47	6.9	0.00	7.3	9.4	11.4	1.7
			6	5	0.43	5.4	0.00	21.1	7.6	10.2	1.7
			7	205	0.42	4.1	0.00	30.9	6.5	9.2	3.9
			8	405	0.38	9.0	0.00	47.4	5.9	8.5	1.8
			9	605	0.30	3.8	0.00	106.2	6.4	7.9	6.0
			10	805	0.57	4.7	0.00	49.7	19.5	10.0	12.4

Units:

Flux, J	[ng(N) $m^{-2}s^{-1}$]
Relative Standard Deviation, STD	[%]
Temperature	[°C]
$[NO_x]$	[ppbv]

TABLE 1 (cont'd)

Soil NO_x Emission Fluxes

Location	Sample	Start Date	Run #	Start Time	J(NO)	STD J(NO)	$J(NO_2)$	STD $J(NO_2)$	Cham. Air Temp.	Soil Temp.	Ambient $[NO_x]$
Egbert	2C	23/04/90	1	1417	1.88	3.4	0.29	11.0	28.3	19.1	10.8
			2	1617	1.14	0.9	0.17	1.1	24.5	18.1	12.6
			3	1817	1.09	3.2	0.07	45.3	17.7	15.7	14.6
			4	2017	0.83	1.4	0.00	37.6	11.2	13.4	14.7
			5	2217	0.72	0.9	0.00	14.1	8.9	11.6	15.5
			6	17	0.69	3.1	0.01	374.2	6.8	10.2	9.2
			7	217	0.64	4.0	0.00	575.9	5.7	9.1	8.4
			8	417	0.63	5.1	0.00	180.2	4.6	8.2	7.3
			9	617	0.64	1.7	0.00	28.8	6.8	7.8	8.7
			10	817	1.30	5.7	0.03	66.0	15.2	9.7	9.5
			11	1017	1.25	3.6	0.04	64.6	24.3	13.9	9.0
			12	1217	0.80	3.6	0.06	18.3	29.1	17.8	0.0
Egbert	3A	25/04/90	1	1425	1.49	2.0	0.11	8.1	35.4	19.2	1.7
			2	1625	1.72	1.2	0.11	13.5	33.1	20.8	1.5
			3	1825	0.21	8.2	0.49	3.4	23.1	20.1	1.4
			4	2025	0.31	7.9	0.57	3.3	18.1	18.2	2.2
			5	2225	0.19	9.1	0.57	1.4	15.4	16.7	1.5
			6	25	0.08	34.3	0.54	2.9	16.1	15.9	1.5
			7	225	0.13	58.7	0.37	12.2	14.1	15.2	1.2
			8	425	0.10	91.4	0.62	7.4	14.2	14.7	1.1
			9	625	0.20	147.2	0.72	31.3	17.1	14.3	1.7
			10	825	0.20	213.5	0.78	37.5	26.8	15.8	1.7
Egbert	3B	01/05/91	1	1221	0.70	5.5	0.19	7.8	18.3	14.7	0.8
			2	1421	0.79	3.0	0.35	2.0	21.6	15.7	2.7
			3	1621	1.68	2.4	0.22	8.2	19.4	15.9	1.1
			4	1821	0.75	2.4	0.22	8.9	12.4	14.5	1.0
			5	2021	0.61	3.0	0.10	16.1	3.7	12.1	0.7
			6	2221	0.40	2.9	0.14	3.9	2.5	10.3	1.0
			7	21	0.35	5.9	0.12	10.9	0.3	8.9	1.1
			8	221	0.38	4.4	0.17	13.8	-0.8	7.8	1.4
			9	421	0.22	9.6	0.10	18.2	0.3	7.1	1.1
			10	621	0.34	0.0	0.16	11.2	5.2	7.1	1.0
			11	821	0.44	3.7	0.12	3.8	14.9	8.2	0.9
			12	1021	0.72	2.7	0.12	16.2	18.7	10.1	0.0
Egbert	3C	02/05/91	1	1224	1.43	3.4	0.00	289.8	17.9	13.3	0.8
			2	1424	0.72	12.8	0.21	4.9	20.0	14.8	1.1
			3	1624	1.04	3.7	0.19	8.4	18.3	15.2	0.9
			4	1824	0.79	3.7	0.13	13.9	9.3	14.0	1.0
			5	2024	0.04	129.3	0.56	10.7	2.5	12.3	1.6
			6	2224	0.17	49.4	1.28	6.6	1.0	10.8	5.4
			7	24	0.39	7.1	0.18	19.5	0.7	9.7	2.1
			8	224	0.27	10.9	0.35	5.1	-0.4	8.7	2.7
			9	424	0.40	12.0	0.21	31.1	-1.4	7.9	3.3
			10	624	0.88	6.3	0.28	19.7	4.9	7.6	7.8
			11	824	0.81	0.9	0.00	141.4	17.9	8.4	1.3
Egbert	3D	03/05/91	1	1109	1.21	1.4	0.00	16.5	16.8	11.3	

Units:

Flux, J	[ng(N) $m^{-2}s^{-1}$]
Relative Standard Deviation, STD	[%]
Temperature	[°C]
$[NO_x]$	[ppbv]

TABLE 2

Diurnal-Average Soil NO_x Emission Fluxes

Location	Sample	Start Date	Diurnal Averages J(NO)	J(NO_2)	Soil T	[NOx]
Borden	1	23/10/89	0.09	0.11	8.3	5.0
Borden	2	24/10/89	0.21	0.15	10.0	11.2
Egbert	1	30/10/89	1.50	1.54	11.3	22.3
Egbert	2B	22/04/90	0.58	0.02	11.8	3.3
Egbert	2C	23/04/90	0.97	0.06	12.9	10.9
Egbert	3A	25/04/90	0.46	0.49	17.1	1.6
Egbert	3B	01/05/91	0.62	0.17	11.0	1.2
Egbert	3C	02/05/91	0.63	0.31	11.1	2.5

Units:

Flux, J	[ng(N) $m^{-2}s^{-1}$]
Relative Standard Deviation, STD	[%]
Temperature, T	[^{o}C]
[NO_x]	[ppbv]

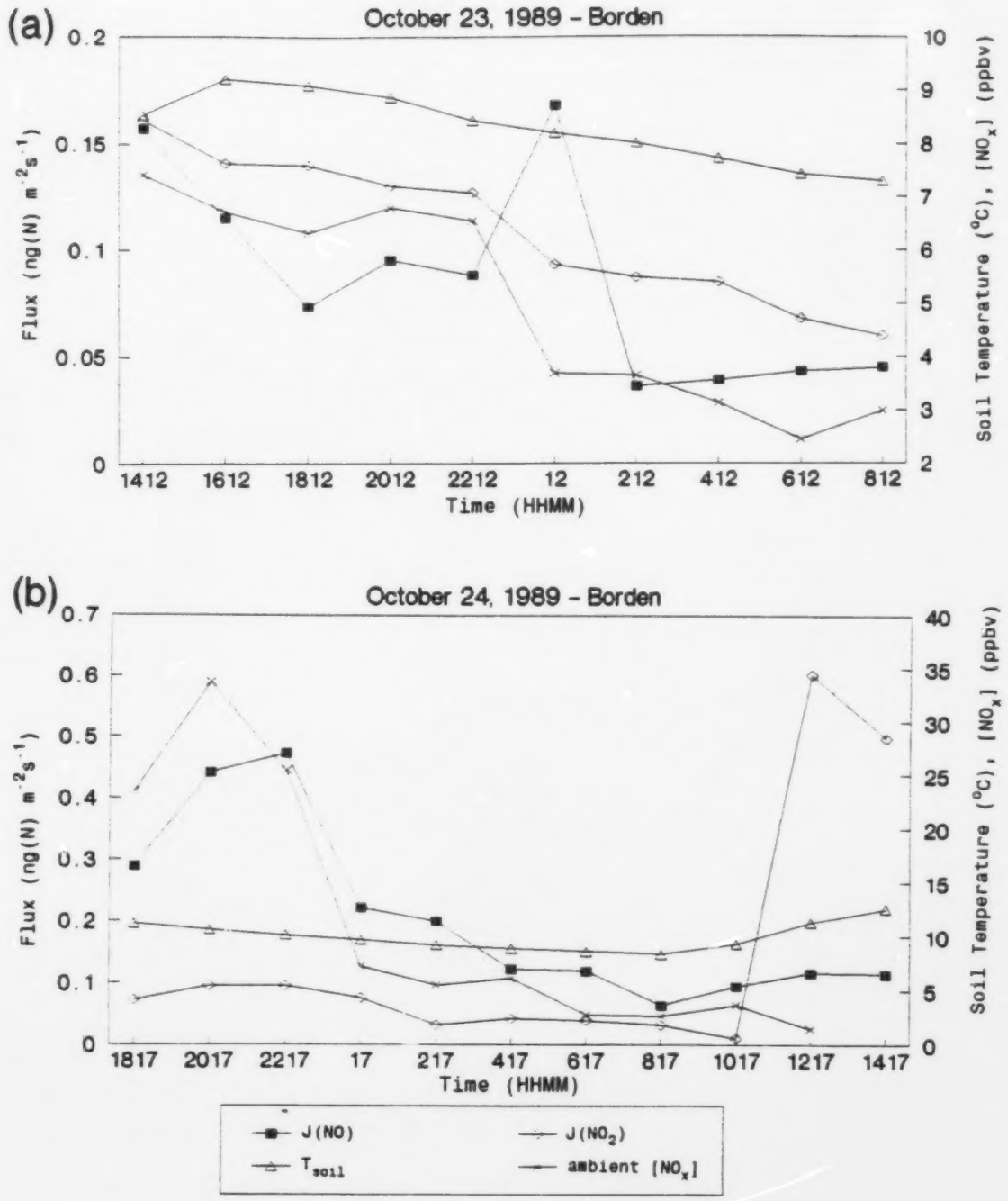

Figure 2. Variation of NO and NO_2 emission fluxes over the diurnal cycle for the tests beginning (a) October 23, 1989, and (b) October 24, 1989, at the Borden forest site. The soil temperature and ambient concentration of NO_x are also shown.

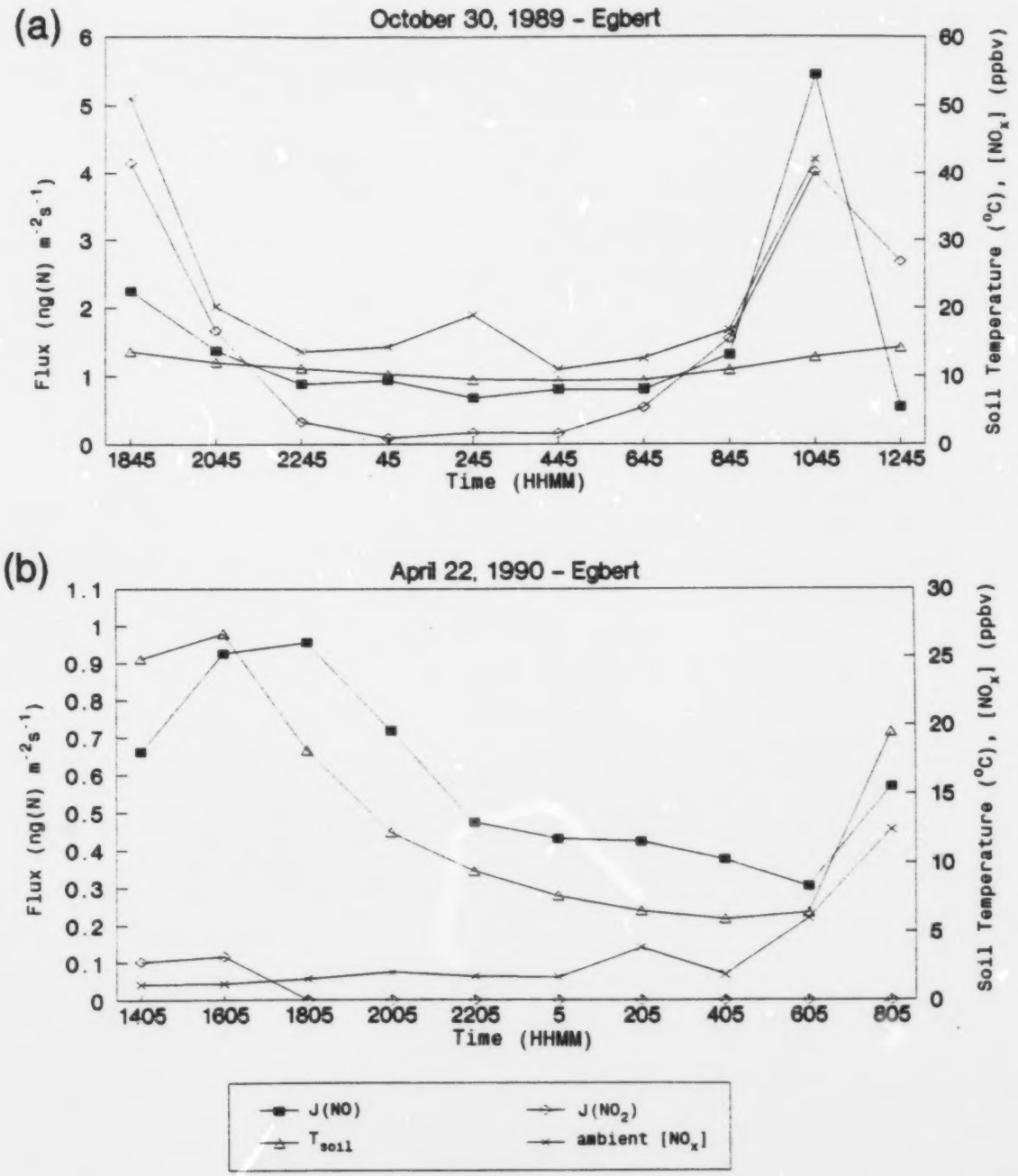

Figure 3. Variation of NO and NO_2 emission fluxes over the diurnal cycle for the tests beginning (a) October 30, 1989, and (b) April 22, 1990, at the Egbert alfalfa field site. The soil temperature and ambient concentration of NO_x are also shown.

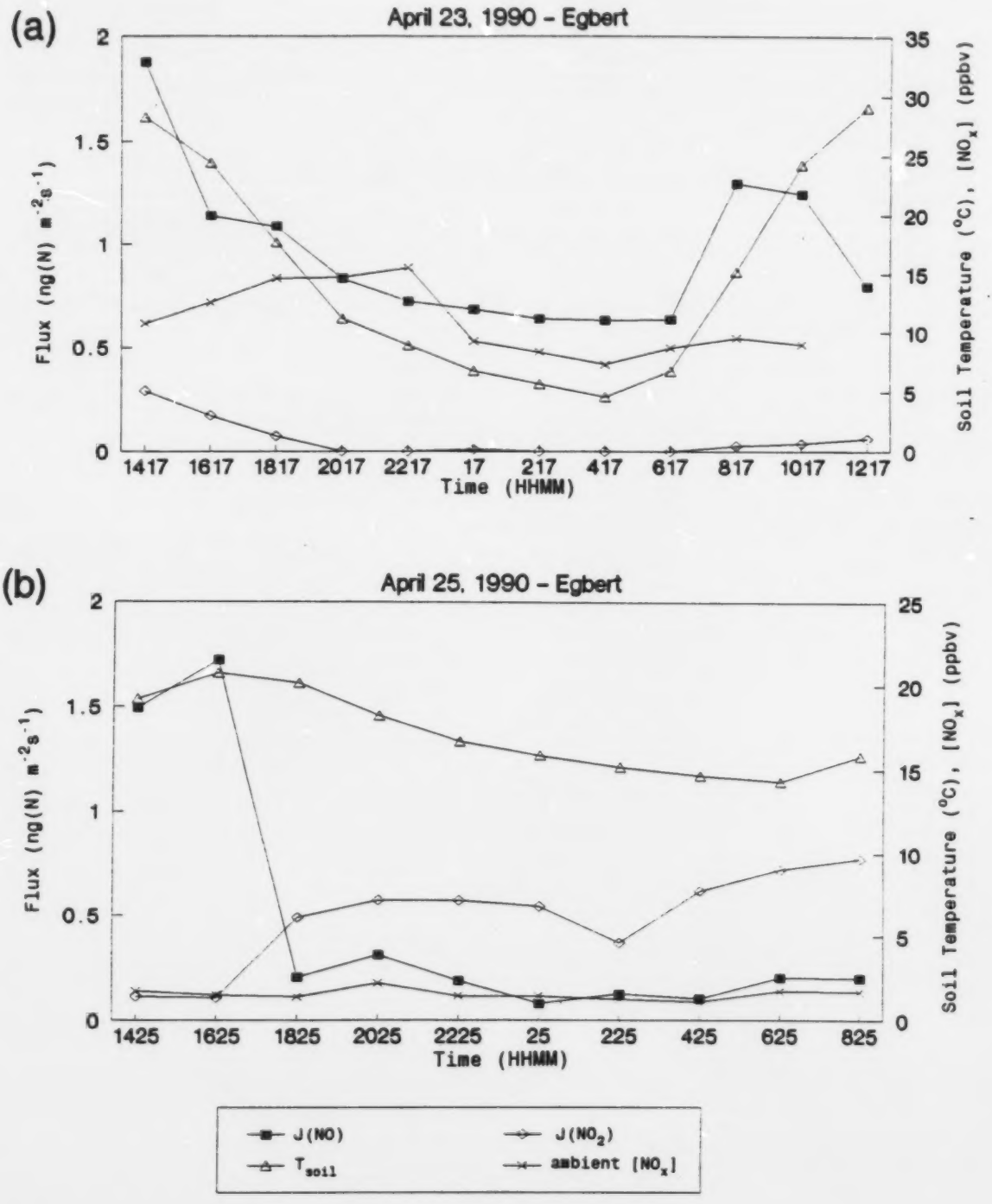

Figure 4. Variation of NO and NO_2 emission fluxes over the diurnal cycle for the tests beginning (a) April 23, 1990, and (b) April 25, 1990, at the Egbert alfalfa field site. The soil temperature and ambient concentration of NO_x are also shown.

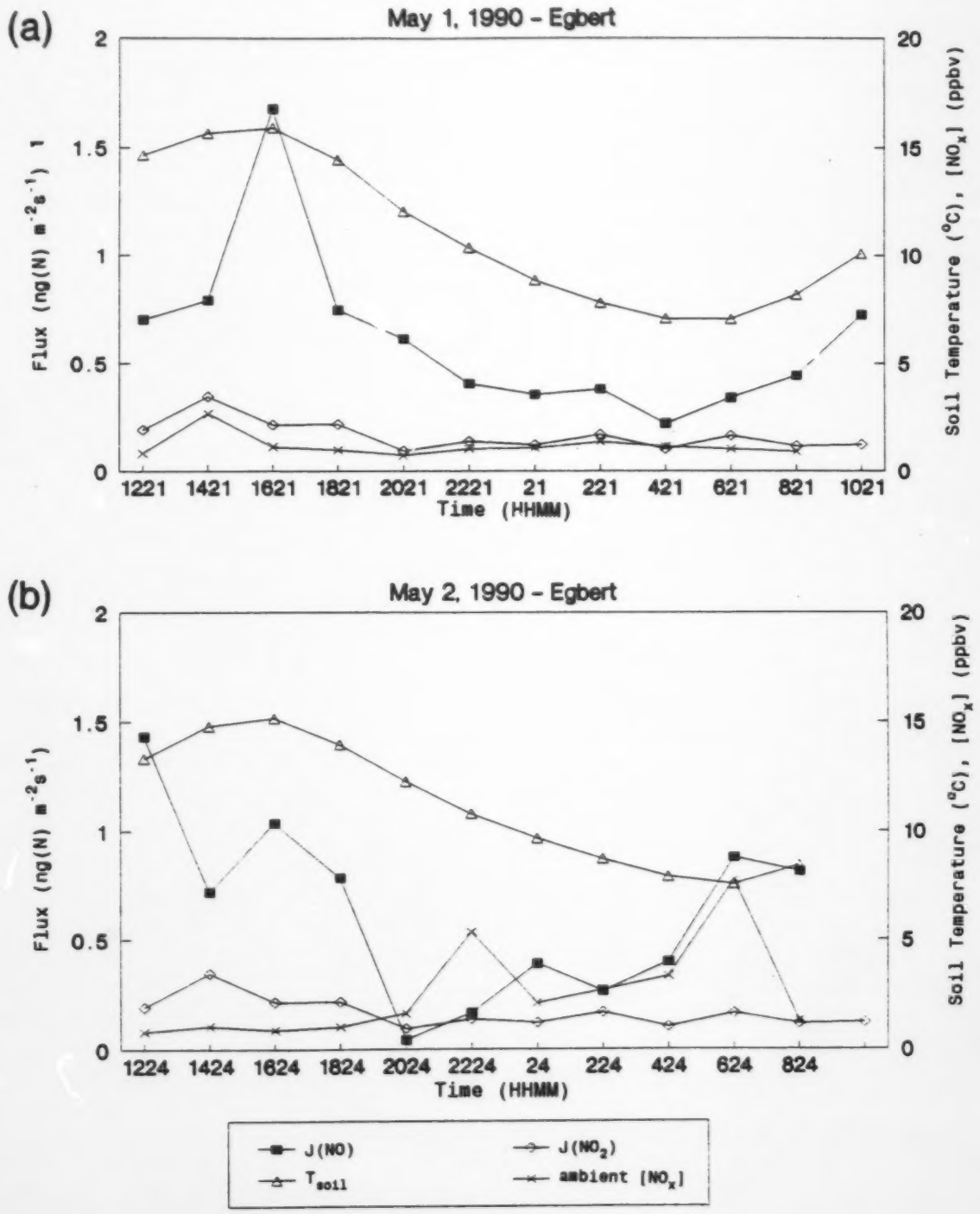

Figure 5. Variation of NO and NO_2 emission fluxes over the diurnal cycle for the tests beginning (a) May 1, 1990, and (b) May 2, 1990, at the Egbert alfalfa field site. The soil temperature and ambient concentration of NO_x are also shown.

that soil temperature is an important controlling variable (eg, Anderson and Levine 1987, Headon et al. 1990). In general, and as found previously, the NO emission flux appeared to follow a similar diurnal cycle to the soil temperature. However, the NO emission flux did not always track the soil temperature. For example, a sharp increase in the emission flux was occasionally observed, as in the October 23 test at Borden and the May 1 test at Egbert. After these bursts of higher flux, the flux returned to a lower value during the next measurement period two hours later. The reason for these apparent bursts of flux is not known.

During the spring, the NO_2 flux was usually lower than the NO flux, consistent with previous measurements where the NO_2 flux was often less than 10% of the NO flux (Mackay and Ogram 1989, Headon et al. 1990). However, the results obtained at both Egbert and Borden during the fall of 1989 proved to be an exception, with NO_2 fluxes being of similar order to, and sometimes greater than, the NO fluxes. In these cases, the trend in the NO_2 flux often did not match the trend in the NO flux, indicating that the fluxes of these two species may originate from different processes or from different stages of a process. (Emissions of NO_2 and NO from soils are believed to originate either from nitrification or denitrification processes, depending on the level of nitrate within the soil, as well as other soil parameters, eg, temperature, moisture content, availability of oxygen, etc., but it is beyond the scope of the present work to attempt to interpret the present results in terms of biochemical mechanisms within the soil. For a discussion of these mechanisms, which in many cases are still poorly understood, see, eg, Firestone and Davidson, 1989).

In some cases, where the observed flux was very small, and ambient levels of NO_x were high, it is conceivable that some part of the observed flux was a result of leakage of ambient air into the chamber, or of re-emission of NO_2 that had diffused into the soil prior to the experimental plot being covered by the chamber. (Residual NO_x in the chamber atmosphere would be expected to be negligible as the flux measurements were made after the chamber had been in the down position for about forty minutes, a time period corresponding to eight times the time constant for air exchange in the chamber.) Figures 2 to 5 also show the ambient NO_x concentration, $[NO_x]$. In some cases, eg, October 23 and 24, the NO emission fluxes appear to track the ambient $[NO_x]$, whereas in other cases, eg, the April/May results at Egbert, there appears to be little correlation. The apparently similar trends in ambient NO_x and the emission fluxes in the October results may thus be coincidence.

4.0 CONCLUDING REMARKS

This report documents measurements of natural NO_x emissions from unfertilized soils in Ontario at a forest site (CFB Borden) and at the Centre for Atmospheric Research Experiments (CARE), Egbert, using a flow-through chamber technique. Experiments were conducted during late October, 1989, and during April and May, 1990.

Measured NO emission fluxes at Borden were small and ranged from 0.04 to 0.47 ng(N) $m^{-2}s^{-1}$ over a two day period in late October, with diurnal average values of 0.09 and 0.21 ng(N) $m^{-2}s^{-1}$, respectively, for each of the two days.

NO emission fluxes measured at Egbert a few days later were higher and ranged from 0.05 to 5.5 ng(N) $m^{-2}s^{-1}$ over a single diurnal cycle, with a diurnally averaged flux of 1.5 ng(N) $m^{-2}s^{-1}$. Fluxes measured in spring at Egbert ranged from 0.04 to 1.9 ng(N) $m^{-2}s^{-1}$ over five days of tests in late April and early May (diurnal averages ranged from 0.46 to 0.97 ng(N) $m^{-2}s^{-1}$). These fluxes, on average, were of similar order to, but somewhat lower than, fluxes measured previously at the same site during the summer and late summer of 1989.

Emission fluxes of NO_2 measured during the autumn of 1989 were occasionally of similar magnitude to the NO fluxes, in contrast to previously reported results, and to the measurements made during spring, 1990 at Egbert, where fluxes of NO_2 were generally smaller than those of NO.

Consistent with previous observations, NO emission fluxes generally followed a diurnal cycle, peaking during the day and reaching a minimum at night. However, occasional bursts of flux were observed, which were uncorrelated with soil temperature.

ACKNOWLEDGEMENTS

We express our appreciation to F. Froude, K. Puckett, H. Neumann and G. den Hartog of Environment Canada (AES), and F.S. Spencer, G.C. Edwards, A. Lemyk and D. Dobrofsky of Ontario Hydro Research Division, for their assistance. Environment Canada is thanked for providing access to the Borden and Egbert experimental sites.

Approved by:

J. Pagel
Manager
Environmental Sciences Department

Prepared by:

for J.W. Middleton
Student
Environmental Physics & Chemistry Section

Reviewed by:

O.T. Melo
Supervising Engineer
Environmental Physics & Chemistry Section

C.L. Ogram
Associate Research Scientist
Environmental Physics & Chemistry Section

REFERENCES

Anderson I.C., and J.S. Levine (1987). "*Simultaneous Field Measurements of Biogenic Emissions of Nitric Oxide and Nitrous Oxide*". Journal of Geophysical Research, 92: 965-976.

Edwards, G.C. (1991). Private communication.

Firestone, M.K., and E.A. Davidson (1989). "*Microbial Basis of NO and N_2O Production and Consumption in Soil*". In "Exchange of Trace Gases between Terrestrial Ecosystems and the Atmosphere", M.O. Andrae and D.S. Schimel, Editors, John Wiley and Sons, Chichester.

Headon, C., A. Lemyk, V.W. Middleton and G.L. Ogram (1990). "*Field Measurements of Natural NO_x Emissions from Soils: Egbert, Ontario, July-September, 1989*". Ontario Hydro Research Division Report 90-120-K.

Johansson C. and Granat L. (1984). "*Emission of Nitric Oxide from Arable Land*". Tellus, 36B: 25-37.

Lin, X. (1989). "*A Study of Ontario Hydro's Contribution to Ozone Levels in Ontario: Phase 1 - Literature Review*". Ontario Hydro Research Division Report 89-235-K.

MacKay, M., and G.L. Ogram (1989). "*The Development of a Method to Measure NO_x Emissions from Soils*". Ontario Hydro Research Division Report 89-164-K.

Melo, O.T., X. Lin and G.L. Ogram (1990). "*The Contribution of NO_x to the Ozone Problem and the Implications for NO_x Controls*". Proceedings of the Canadian Electrical Association (CEA) Engineering and Operating Division Meeting, Montreal, March 25-29.

Neumann, H.H., G. den Hartog and R.H. Shaw (1989). "*Leaf Area Measurements based on Hemispheric Photographs and Leaf Litter Collection in a Deciduous Forest during Autumn Leaf-Fall*". Agricultural Meteorology, 45: 325-345.

Parrish, D.D., E.J. Williams, D.W. Fahey, S.C. Liu and F.C. Fehsenfeld (1987). "*Measurement of Nitrogen Oxide Emissions from Soils: Intercomparison of Enclosure and Gradient Measurement Techniques*". Journal of Geophysical Research, 92: 2165-2171.2

Shepherd, M.F., S. Barzetti and D.R. Hastie (1991). "*The Production of Atmospheric NO_x and N_2O from a Fertilized Agricultural Soil*". Atmospheric Environment, 25A: 1961-1969.

Wiliams, E.J., D.D. Parrish and F.C. Fehsenfeld (1987). "*Determination of Nitrogen Oxide Emissions from Soils: Results from a Grassland Site in Colorado, United States*". Journal of Geophysical Research, 92: 2173-2179.

APPENDIX A

SOIL PROPERTIES

Table A1: Soil Chemical Analysis for Soil NO_x Emission Studies at Borden and Egbert, October, 1989 and April-May, 1990.

BORDEN:

Agri-Food Laboratories analysis:

Sample	pH	P (ppm)	K (ppm)	Mg (ppm)	Ca (ppm)	NO3-N (ppm)	C.E.C. (meq/100g)	Organic Matter (% by Wt)
1	6.10	26	69	111	2637	6	15.49	4.60
2	5.65	24	75	98	1881	2	17.61	5.40

University of Guelph analysis:

Sample	pH	P (mg/kg)	K (mg/kg)	Mg (mg/kg)	Ca (mg/kg)	NH4-N (mg/kg)	NO3-N (mg/kg)	C.E.C. (meq/100g)	Organic Matter (% by Wt)
1	6.4	26	289	94	2730		5.63	10.8	5.0
2	5.7	31	170	112	1860		6.41	14.4	6.4

EGBERT:

Agri-Food Laboratories analysis:

Sample	pH	P (ppm)	K (ppm)	Mg (ppm)	Ca (ppm)	NO3-N (ppm)	C.E.C. (meq/100g)	Organic Matter (% by Wt)
1A	5.98	10	71	99	3062		17.52	5.2
1B	6.37	10	59	80	2764		15.84	5.2
2A	6.7	7	25	40	1382	6	9	2.9
2B	7.2	8	27	42	1793	2	11	2.5
2C	7.1	13	23	42	1680	4	10	2.8
3A	7.4	6	23	90	1822	8	11	3.1
3B	7.2	9	30	96	1722	4	11	3.0
3C	7.3	9	24	96	1773	6	11	3.0
3D	6.6	12	26	90	1499	4	10	4.0

University of Guelph analysis:

Sample	pH	P (mg/kg)	K (mg/kg)	Mg (mg/kg)	Ca (mg/kg)	NH4-N (mg/kg)	NO3-N (mg/kg)	C.E.C. (meq/100g)	Organic Matter (% by Wt)
1A						8.15	12.64		
1B						6.24	5.04		
2A	6.86	8	28	44	2870	6.54		14.7	2.7
2B	7.53	5	27	79	3120	3.60		16.3	1.9
2C	7.03	16	28	34	3060	7.03		17.4	2.4
3A	7.35	8	34	82	3140	5.15		16.4	2.4
3B	6.74	6	24	44	2890	8.75		15.9	2.6
3C	7.27	7	35	100	3460	6.32		14.6	1.9
3D	6.59	9	33	107	2610	7.10		13.9	2.4

Table A2: Soil Texture for Soil NO_x Emission Studies at Borden and Egbert, October, 1989 and April-May, 1990.

Location	Sample	Agri-Food Laboratories Analysis			University of Guelph Analysis		
		Sand (% by Wt)	Silt (% by Wt)	Clay (% by Wt)	Sand (% by Wt)	Silt (% by Wt)	Clay (% by Wt)
Borden	1	81.0	13.0	6.0	86.2	8.4	5.5
	2	83.0	11.0	6.0	84.3	9.9	5.8
Egbert	1						
	2	68.00	22.00	10.00	69.2	25.3	5.5
	3	76.00	18.00	6.00	74.5	21.3	4.3

TABLE A3: Soil Mass/Volume Analysis for NO_x Emission Studies at Borden and Egbert, October, 1989 and April-May, 1990.

Location	Sample	Soil Mass (g)	Water Mass (g)	Soil Volume (%)	Water Volume (%)	Free Pore Volume (%)
Borden	1-I	68.88	15.97	27.58	16.94	55.48
	1-O	88.32	20.84	35.36	22.11	42.53
	2-I	73.95	21.87	29.61	23.20	47.19
	2-O	87.07	24.93	34.86	26.45	38.69
Egbert	1A-I					
	1A-O					
	1B-I					
	1B-O					
	2A-I					
	2A-O	266.63	49.15	41.36	20.20	38.44
	2B-I	181.42	28.11	45.02	18.49	36.49
	2B-O	186.98	30.29	46.40	19.92	33.67
	2C-I	186.76	29.38	46.35	19.32	34.33
	2C-O	190.51	30.95	47.28	20.36	32.36
	3A-I	156.60	21.64	38.87	14.23	46.90
	3A-O	158.30	21.81	39.29	14.34	46.37
	3B-I	132.83	13.24	32.97	8.71	58.33
	3B-O	153.11	13.69	50.66	12.00	37.33
	3C-I	151.45	14.83	37.59	9.75	52.66
	3C-O	147.75	15.51	36.67	10.20	53.13
	3D-I	167.92	21.73	41.67	14.29	44.03
	3D-O	156.31	19.96	38.79	13.13	48.08

Sample Designation:
I - From test plot (inside chamber).
O - Adjacent to test plot.